

**FRAMEWORK SOLIDS, MESOPHASES AND
NANOSTRUCTURES
OF
ORGANICALLY TEMPLATED
VANADIUM AND MOLYBDENUM PHOSPHATES**

by
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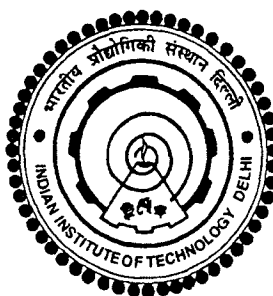
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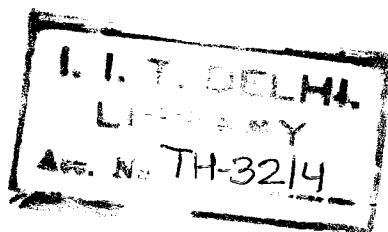
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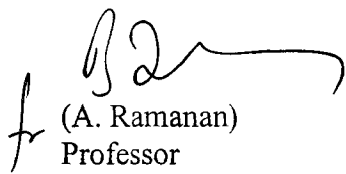


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CERTIFICATE

This is to certify that the thesis entitled **“Framework Solids, Mesophases And Nanostructures Of Organically Templated Vanadium And Molybdenum Phosphates”** being submitted by **Ms. Minakshi Asnani** to the Indian Institute of Technology, New Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her. Ms. Minakshi Asnani has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which, to my knowledge has reached requisite standard.

The results contained in the dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.


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Dedicated to my parents

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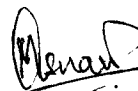
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ABSTRACT

An extensive contemporary interest in the properties and applications of framework solids has spurred significant activity in the design of synthetic phases. Transition metal phosphates constitute an important family of such solids and significant interest in these materials is mainly because of potential catalytic properties and flexibility to tune pore dimensions (microporous, mesoporous and nanoporous). It is now recognized that slight variations in the synthetic conditions, particularly the organic component can dramatically influence structures of the inorganic phosphates in the resultant composite materials. These chemical precursors might act as structure directing agents, charge compensators or space fillers facilitating the formation of open or porous networks with high specific surface area that have structural and functional analogies with zeolites. Rational design and synthesis of crystalline hybrid materials is still in its infancy despite vast amount of work that has been carried out on the preparation of new structures. Understanding the driving force behind the formation of organic/inorganic solids still remains a formidable challenge and is an area of contemporary research.

The present study is an attempt to form new vanadium phosphate (*VPO*) and molybdenum phosphate (*MoPO*) based solids. The thesis is divided into four chapters and describes synthesis, characterization, ion exchange and magnetic properties of organically templated *VPOs* and *MoPOs*. We have investigated the structure directing influence of several templates such as aromatic diamine (pyridazine), transition metal complex $\{\text{Co}(\text{en})_3\}$, cationic surfactants (dodecylpyridinium chloride, cetylpyridinium chloride, cetyltrimethylammonium bromide) and ethylenediamine (*en*).

The solids synthesized in this study have been characterized by single crystal and powder X-ray diffraction, SEM/EDAX, TGA/DTA, low temperature magnetic

susceptibility measurements, AFM, TEM, CP-MAS solid state NMR and BET measurements.

We have been successful in isolating many new *VPO* solids. The templating influence of pyridazine by exploiting π - π interactions led to the isolation of the first example of a mixed valent vanadium (III, IV) phenylphosphonate. The use of a chiral transition metal complex, $[\text{Co}(\text{en})_3]^{3+}$, yielded a vanadium borophosphate solid where only one enantiomer of the metal complex and the cluster $[\text{V}_3\text{BP}_3\text{O}_{19}]^{5-}$ were involved. The occurrence of only one enantiomer of the metal complex suggests molecular recognition ability of the inorganic host. Subtle changes in synthetic conditions in the presence of $[\text{Co}(\text{en})_3]^{3+}$ resulted into a thermodynamically stable mixed valent vanadyl phosphate, *enVPO*, which exhibited unusual ion exchange reactivity.

With monovalent ions (K^+ , Rb^+ , Ti^+ , NH_4^+), novel topotactic exchange reactions of *enVPO* were achieved at room temperature. A new metastable phase, $\text{Ti}_{0.45}\text{V}^{\text{IV/V}}\text{OPO}_4 \cdot 0.33\text{H}_2\text{O}$, was obtained. Reaction of *enVPO* with silver ions resulted into a new silver vanadium phosphate, $\text{Ag}_{3.5}\text{V}^{\text{V}}\text{P}_{1.5}\text{O}_8$, coated with silver nanoparticles ($\sim 15\text{nm}$) which on heating above 400°C yielded a 2:1 mixture of two thermodynamically stable phases, $\text{Ag}_2\text{VO}_2\text{PO}_4$ and Ag_3PO_4 . Alkali metal intercalated layered vanadyl phosphates showed interesting low temperature magnetic interactions.

The templating behavior of a cationic surfactant, dodecylpyridinium chloride (DPC), was investigated for the first time. Hydrothermal reactions with high concentration of DPC formed lamellar *VPO* mesophases with high surface area.

Soft chemistry routes enabled us to obtain nanostructured *VPO*s. Under ambient conditions, reactions with DPC formed *VPO* nanorods (width = 40-60nm, length = 0.2-1 μm). On the basis of detailed TEM and AFM studies, a plausible seed growth

mechanism for the formation of **VPO** nanorods is suggested. Effect of reaction parameters such as concentration of reactants, pH and aging time on the morphology of **VPO** nanophases was investigated. The process seems to offer a low temperature, low cost and convenient way of obtaining single phasic **VPO** nanorods. In addition, other surfactants such as cetylpyridinium chloride, cetyltrimethylammonium bromide and their mixtures were found to be effective in obtaining **VPO** nanophases.

The structure directing effect of *en* on the formation of novel hybrid **MoPO** structures was explored. Organic acids (succinic acid, oxalic acid and glycine) were helpful to produce reduced **MoPOs**. Under hydrothermal conditions, *en* alone was efficient to reduce molybdenum core in the pH range 4-6, forming a biphasic mixture of $\text{Na}(\text{Mo}^{\text{V}}_6\text{P}_4\text{O}_{31})_2$ and $\text{Mo}^{\text{VI}}_5\text{P}_2\text{O}_{23}$. The mild reducing agent, succinic acid was ineffective for the synthesis of monophasic reduced molybdenum species, $\text{Na}(\text{Mo}^{\text{V}}_6\text{P}_4\text{O}_{31})_2$. The stronger reducing agent, oxalic acid, led to the isolation of single phasic $\text{Na}(\text{Mo}^{\text{V}}_6\text{P}_4\text{O}_{31})_2$ species at neutral pH. However, in presence of glycine pure $\text{Na}(\text{Mo}^{\text{V}}_6\text{P}_4\text{O}_{31})_2$ solids were obtained in a broad range of pH (1-9). Four new $\text{Na}(\text{Mo}^{\text{V}}_6\text{P}_4\text{O}_{31})_2$ structures (0D, 1D and 2D) with different connectivities of sodium cation and varying degrees of protonation were isolated. At highly alkaline conditions (pH above 9), a novel layered sodium hydrogenphosphate solid intercalated with *en* was crystallized. Thus, pH and organic template were found to be critical in controlling the dimensionality of **MoPO** framework.

The emerging structural rationalization on the basis of the results obtained in this study suggests that as the database continues to evolve, correlation of structure, reactivity and properties will become more apparent.

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